

PETI-298 PREPARED BY MICROWAVE SYNTHESIS: NEAT RESIN AND COMPOSITE PROPERTIES

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ABSTRACT

PETI-298 is a high temperature/high performance matrix resin that is processable into composites by resin transfer molding (RTM), resin infusion and vacuum assisted RTM techniques. It is typically synthesized in a polar aprotic solvent from the reaction of an aromatic anhydride and a combination of diamines and endcapped with phenylethynylphthalic anhydride. Microwave synthesis of PETI-298 was investigated as a means to eliminate solvent and decrease reaction time. The monomers were manually mixed and placed in a microwave oven for various times to determine optimum reaction conditions. The synthetic process was subsequently scaled-up to 330g. Three batches were synthesized and combined to give 1 kg of material that was characterized for thermal and rheological properties and compared to PETI-298 prepared by the classic solution based synthetic method. The microwave synthesized PETI-298 was subsequently used to fabricate flat laminates on T650 carbon fabric by RTM. The composite panels were analyzed and mechanical properties determined and compared with those fabricated from PETI-298 prepared by the classic solution method. The microwave synthesis process and characterization of neat resin and carbon fiber reinforced composites fabricated by RTM will be presented.

KEY WORDS: Resin Transfer Molding, High Temperature Polymers, Phenylethynyl Terminated Imides, Microwave Synthesis

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1. INTRODUCTION

There is a need for thermally stable high performance resins that are processable by resin transfer molding (RTM) and resin infusion for applications requiring use temperatures above 288°C on advanced aerospace vehicles and jet engines. These potential applications are in and around hot areas on the vehicle and engines. Some of the criteria that the materials need to meet to be processable by these techniques (i.e., RTM) are low and stable melt viscosity (i.e., <3 Pa·s), cure without volatile evolution, low cost, and low toxicity. To be useful in the aforementioned applications, the composites need to display high cured glass transition temperature (T_g , i.e. $>290^\circ\text{C}$), micro crack resistance and good mechanical performance with high retention of mechanical properties under conditions dictated by the service environment of the vehicle throughout its operational lifetime. This service environment may include high temperature, high stress, object impact, thermal cycling, and exposure to moisture and aircraft fluids. By leveraging work performed under NASA's High Speed Civil Transport Program in the late 1990's on phenylethynyl terminated imide (PETI) oligomers, a family of resins was developed that met these criteria [1-4]. One of these resins was PETI-298 with a cured T_g of $\sim 300^\circ\text{C}$ [2]. This resin has been fabricated into composites by RTM and vacuum assisted RTM [5] and evaluated. The composites have exhibited high mechanical properties up to 288°C with good retention of composite properties after aging for 1000 hrs at 288°C in flowing air [2,5]. Additionally, PETI-298/nanosilicate carbon fiber reinforced laminates have been fabricated and characterized [6]. Composite components that are part of an integrated composite tank design for a reusable launch vehicle have been fabricated using PETI-298 [7].

These RTMable resins have been prepared using the classic solvent-based synthetic approach [1-4]. This method involves the reaction of a mixture of diamines with the dianhydride and phenylethynylphthalic anhydride endcapper in a polar aprotic solvent such as N-methyl-2-pyrrolidinone (NMP) to form the amide acid intermediate. The amide acid is subsequently converted to the corresponding PETI by azeotropic distillation with toluene. The resin powder is isolated by pouring the reaction mixture into water, washing in warm water, and drying at $\sim 125^\circ\text{C}$ in flowing air. This process is time consuming and generates hazardous waste that must be properly disposed. Both of these factors as well as others contribute to the final cost of the resin.

One approach of addressing resin cost is the utilization of microwave-assisted organic chemistry to reduce reaction time and waste generation. This is an area of chemistry that began in the 1980's. The method has been successfully employed in the synthesis of many compounds [8]. The main attributes of this approach are improved yields, reduction in reaction times and side products, and quantity of solvent employed. In polymer chemistry, this method has been utilized in bulk radical polymerization of vinyl monomers [9], curing of thermosetting resins (e.g., epoxies) [10], and conversion of poly(amide acid)s to polyimides [11]. Recently, microwave

chemistry has been utilized in the preparation of polyimides in the presence of a small amount of solvent (e.g., m-cresol, dimethylformamide) [12-15]. Solvent-free microwave preparation of phthalimides though has been reported with and without the addition of a catalyst [16]. The objective of the work reported herein was to prepare PETI-298 by the microwave process in the solid state and compare the physical properties of the uncured resin and the mechanical properties of the composites of the cured material to that of PETI-298 prepared by the classical amide acid approach.

2. EXPERIMENTAL

2.1 Starting Materials The following chemicals were obtained from the indicated sources and used without further purification: 1,3,4-APB (Chriskev Co., m.p. 115°C), 3,4'-oxydianiline (3,4'-ODA, Mitsui Petrochemical Ind., Ltd., m.p. 84°C), 4-Phenylethynylphthalic anhydride (PEPA, Imitec, Inc. or Daychem Laboratories, Inc., m.p. 152°C), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA, m.p. 227°C, Allco Chemical Co.). PETI-298 prepared by the classic amide acid method was obtained from Eikos Inc. (Lot# NL17-009) [17]. All other chemicals were used as received without further purification.

2.2 Microwave Synthesis of PETI-298 PETI-298 was prepared at a calculated number average molecular weight (\bar{M}_n) of 750 g/mol by the reaction of the appropriate quantities of 1,3,4-APB (75 mole%) and 3,4'-ODA (25 mole%) with s-BPDA and PEPA. The molecular weight calculation does not include the molecular weight of the endcapping agent. Into a glass beaker (5 X 11 cm) were placed 1,3,4-APB (3.84g, 13.15 mmol), 3,4'-ODA (0.8767g, 4.384 mmol), s-BPDA (2.4711g, 8.4 mmol) and PEPA (4.524g, 18.24 mmol). The solid mixture was physically mixed and subsequently placed in a domestic microwave oven (output = 600 W). The height of the mixture was approximately 1 cm. Reaction times were 10, 15, and 20 min. After completion of the reaction, the solid was pulverized in a mortar and pestle. PETI-298 was prepared in a 1 kg quantity using the method described and a reaction time of 15 min.

2.3 Composite Specimens Quasi-isotropic 8-ply panels were fabricated by infiltrating un-sized T650-35 8 harness satin (HS) carbon fiber fabric on an Invar tool with PETI-298 using a high temperature injector. The sizing on the carbon fiber was removed by a 0.5 to 1 hr hold at 288°C under vacuum prior to injection. The injector designed and built by Radius Engineering according to Lockheed Martin specifications, operates at a maximum temperature of 288°C, flow rate of 500 cc/min, and pressure of 2.75 MPa. The tool containing the fabric was loaded into a press, heated to 288°C, and held at 288°C for 0.5 to 1 hr prior to resin injection. PETI-298 was degassed in the injector by heating to 288°C and holding for 1 hr prior to injection. The degassing step is generally required in RTM primarily to remove moisture, residual solvent, and air from the resin. The molten resin was used to infiltrate 8-ply stacks of un-sized T650-35 8HS fabric with [+45/0/90/-45]_s orientation in an Invar tool. The tool was clamped in the press in

order to assure adequate sealing. After the resin was injected at 288°C at a rate of 200 cc/min, the part was held at a minimum of 1.34 MPa of hydrostatic pressure and heated to 371°C and held at 371°C for 1 hr + 10 min. The 33 cm x 36 cm laminates were cooled in the mold. The laminates were ultrasonically scanned (C-scanned, pulse echo), cut into specimens, and tested for mechanical properties. The panels were examined for microcracks by a microscope up to 400X magnification. Resin content, fiber volume, and void content were determined by acid digestion using a 1:1 (w/w) solution of concentrated sulfuric acid and 30% hydrogen peroxide. Open hole compression (OHC) properties (Northrup Grumman Test [18]) were determined on specimens 22.9 cm by 3.81 cm with a 0.64 cm hole in the center. Short beam shear (SBS) strength (ASTM D2344-84) was determined on specimens 0.64 cm by 1.91 cm. Five specimens were tested under each condition.

2.4 Other Characterization Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the T_g taken at the inflection point of the ΔH versus temperature curve. The cured T_g was determined by heating the sample to 371°C in an open aluminum pan and holding for 1 hr. The sample was cooled and subsequently re-heated to record the T_g. Dynamic thermogravimetric analysis (TGA) was performed on uncured imide powder in air at a heating rate of 2.5 °C/min and a flow rate of 50 mL/min. The samples were heated to 100°C at 20°C/min, held for 0.5 hr and subsequently heated to 600°C at 2.5°C/min. Gel permeation chromatography (GPC) was performed on a Waters 150C system equipped with a model 150R differential viscosity detector and a differential refractive index detector. GPC analyses were performed on dilute solutions of the amide acids and imide powders in freshly distilled NMP containing 0.02 M lithium bromide. The analyses were performed using a two column bank consisting of a linear Waters Styragel HT 6E column covering the molecular weight range of 10³ to 10⁷ g/mole in series with a Styragel HT 3 column covering the molecular weight range of 10² to 10⁴ g/mole. A universal calibration curve was generated with Polymer Laboratories narrow molecular weight distribution polystyrene standards having molecular weights ranging from 500 to 2.75 x 10⁶ g/mole. Rheological measurements were conducted on a Rheometrics System 4 rheometer at a heating rate of 4°C/min. Specimen discs (2.54 cm in diameter and 1.5 mm thick) were prepared by compression molding imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a variable strain and a fixed angular frequency of 100 rad/sec while the lower plate was attached to a transducer, which recorded the resultant torque. Storage (G') and loss (G'') moduli and complex melt viscosity (η^*) as a function of time (t) were measured at several temperatures.

3. RESULTS AND DISCUSSION

3.1 Microwave and Classic Amide Acid Synthesis of PETI-298

PETI-298 has been prepared by the classic amide acid route at a calculated \overline{M}_n of 750 g/mol. By this approach, the diamines (1,3,4-APB and 3,4'-ODA) were initially dissolved in NMP with subsequent addition of the dianhydride (s-BPDA) and PEPA as a slurry in NMP (Fig. 1). The mixture was stirred for several hrs at ambient conditions. Subsequent conversion of the phenylethynyl terminated amide acid oligomer to that of the corresponding imide oligomer was accomplished by azeotropic distillation in the presence of toluene. The PETI-298 oligomer remained in solution during cyclodehydration and upon cooling to $\sim 60^\circ\text{C}$. The powder was isolated by pouring the reaction mixture into water to precipitate the oligomer followed by washing in water and drying.

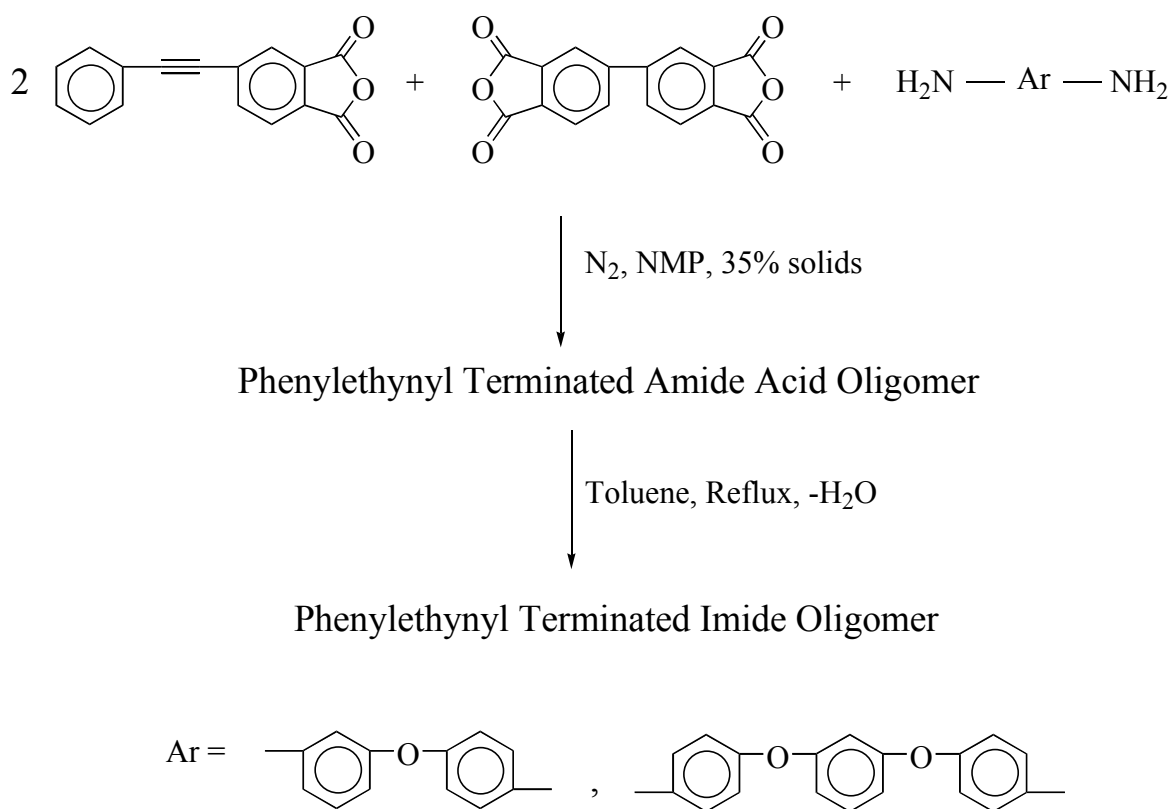


Figure 1: Classical Synthesis of PETI-298

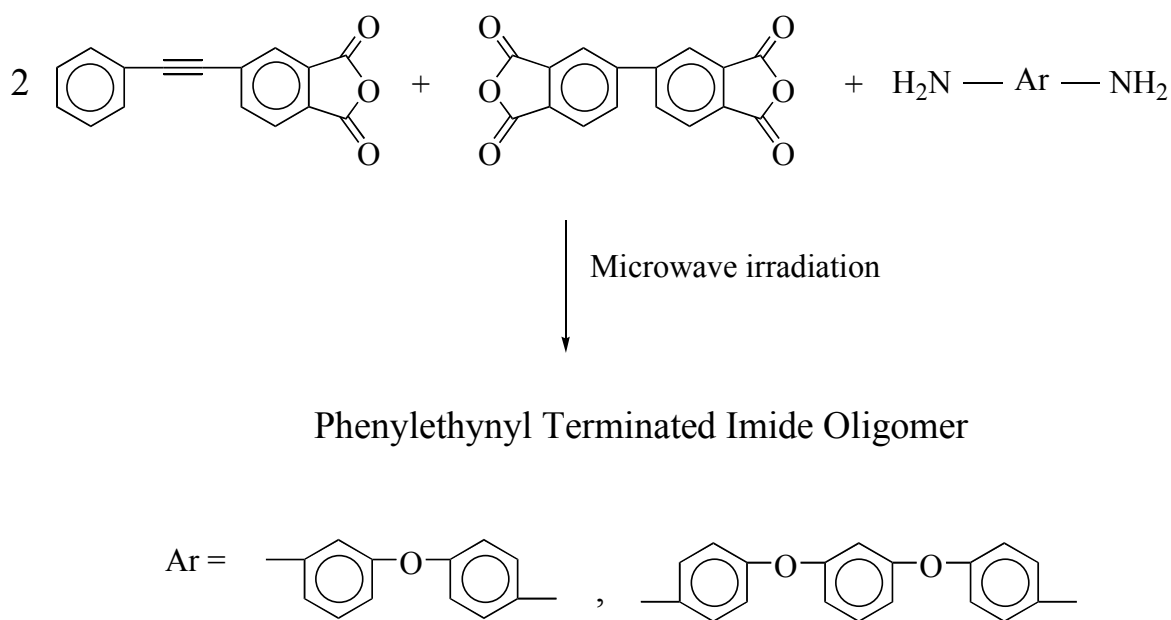


Figure 2: Microwave Synthesis of PETI-298

The microwave synthesis of PETI-298 involved the mechanical mixing of the reactants to form a homogeneous solid mixture of powders. No solvents were added to the mixture. The mixture was then placed into a domestic microwave oven and heated for various times. Times of 10, 15, and 20 min were investigated to determine the optimal reaction duration, which corresponded to the samples TU10, TU15, and TU20, respectively. The reactions progressed through the solid state with the only by-product being water that was generated from the imidization process. Sample TU10 did not go through a melt state and afforded an inhomogeneous dark grey solid. Upon grinding the solid in a mortar, a yellow solid was obtained. TU15 proceeded through a homogeneous melt state during preparation and afforded a yellow powder after grinding. A third sample (TU20) was microwaved an additional 5 min to determine the effect of additional reaction time upon the reaction. Once the dark brown liquid cooled, a yellow powder was obtained after grinding. The thermal properties of PETI-298 prepared by the microwave and classic amide acid routes are presented in Table 1. The microwave prepared samples exhibited lower initial Tgs and several melt transitions (Tms) whereas the classically prepared PETI-298 did not exhibit any Tm. TU10 had a much lower Tg than TU15 and TU20 suggesting that the reaction did not proceed to completion. This assumption is further supported by the results of the TGA data on TU10 that showed much greater weight loss at the various temperatures. TU15 exhibited negligible weight loss (<0.2%) at the various temperatures while TU20 showed no wt loss. The 1% wt loss for TU15 occurred at a slightly lower temperature compared to TU20. However, the initial Tg and Tms of these 2 samples were comparable. After curing powdered samples in the DSC for 1 hr at 371°C, TU15 and TU20 exhibited cured Tgs that were 10°C

Table 1. Thermal Analysis of PETI-298 Oligomers

SAMPLE	Tg (Tm), °C		Total % wt. loss			1 % wt.
	Initial	Cured	250°C	300°C	350°C	Loss, °C
TU10	66 (128, 170, 208, 234)	304	1.9	2.03	2.15	198
TU15	123 (169, 223, 262)	308	0.05	0.07	0.16	433
TU20	124 (168, 228, 265)	308	0	0	0	445
PETI-298	139	298	0	0.08	0.30	450

greater than the cured PETI-298 prepared by the classical method. TU10 had a lower cured Tg compared to the other 2 microwave prepared samples are attributed to incomplete reaction.

3.2 GPC GPC analyses were performed on PETI oligomers to assess molecular weight and molecular weight distribution. Due to the high stoichiometric offsets in the preparation of these materials, the samples exhibited multi-modal molecular weight distributions regardless of the preparative method (Fig. 3). In all cases, the GPC results indicated \bar{M}_n s significantly higher than that calculated (i.e., 750 g/mol). The polydispersities (\bar{M}_w / \bar{M}_n) were significantly less than the theoretical value of 2. The absolute molecular weight data for the imide oligomers is presented in Table 2. As indicated by the data, all the samples had comparable molecular weight values and polydispersities. However, differences in the TU10 chromatogram were evident compared to TU15 and TU20. The chromatograms of TU15 and TU20 were comparable to one another as well as to that of PETI-298 prepared by the classic solution route. However, TU15 and TU20 exhibited a slightly higher proportion of lower molecular weight species and a slightly lower amounts of higher molecular weight species compared to the classically prepared PETI-298 (Fig. 3).

Table 2. GPC Characterization of PETI-298 Oligomers

SAMPLE	\bar{M}_n , g/mole	\bar{M}_w , g/mole	\bar{M}_z , g/mole	\bar{M}_w / \bar{M}_n
TU10	2220	2730	3370	1.23
TU15	2190	2640	3230	1.21
TU20	2280	2770	3410	1.21
PETI-298	2300	2790	3390	1.21

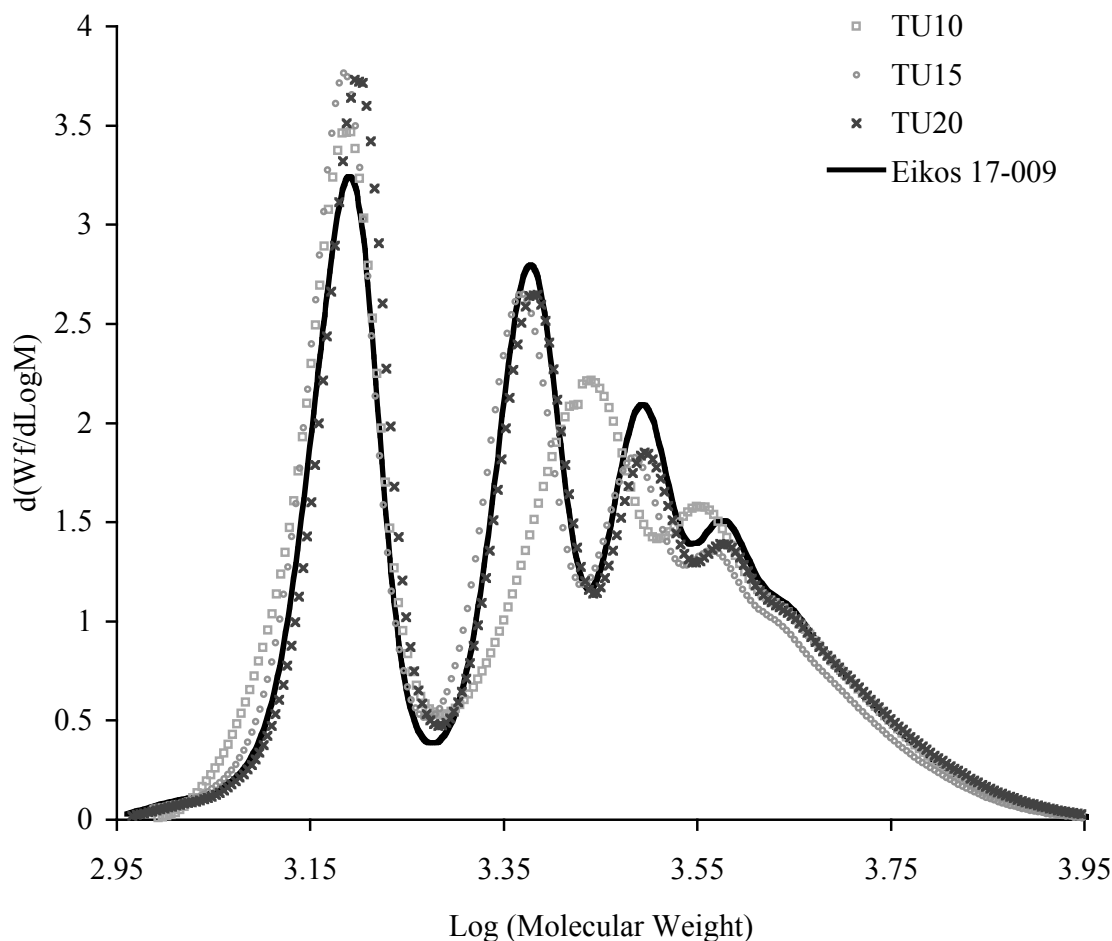


Figure 3: Chromatographs of PETI-298 prepared by microwave and classic solution based synthetic routes.

3.3 Rheology Dynamic rheological properties, G' (t) and G'' (t), were measured using discs compression molded at room temperature. The test chamber of the rheometer was at room temperature prior to specimen introduction. The specimen was heated from 23 to 280°C at a heating rate of 4°C/min and held for 2 hr to assess melt stability. It was then heated to 371°C at the same heating rate and held for 0.5 hr in air. The results of PETI-298 prepared by both approaches, tabulated in Table 3, are initial complex melt viscosities (η^*) and after 2 hrs at 280°C, respectively. The η^* , initially and after the 2 hr hold, of TU15 and TU20 was $\sim 2\times$ that of PETI-298 prepared by the classical route. The values for TU10 was comparable to that obtained for the classical method. Regardless of the preparative method, it is important to note that the PETI oligomers have exhibited excellent melt stability at 280°C. This stability is attributed to the low reactivity of the phenylethynyl groups at this temperature. Consequently, the melt viscosities of these materials are stable for >2 hrs at this temperature.

Table 3. Complex Melt Viscosity of PETI-298 Oligomers

SAMPLE	initial η^* @ 280°C, Pa·s	η^* at 280°C after 2hr hold, Pa·s
TU010	0.4	1.4
TU015	1.2	2.8
TU020	1.2	3.3
PETI-298	0.6	1.4

3.3 Composites Based on the above results, three 330g batches of PETI-298 were prepared using the 15 min microwave cycle and combined. The batch size of the PETI-298 was limited to 330g due to the size constraints of the microwave oven. The neat resin properties of this scaled-up material are compared to that of TU15 (small batch) and PETI-298 prepared by the classic solution route (Table 4). The scaled-up TU15 exhibited initial Tg (T_m), cured Tg, and % wt loss comparable to the small batch. The higher %wt loss at 250°C may be due to absorbed moisture. As previously mentioned, the GPC data for the small microwave prepared (TU15) and the classic amide acid prepared materials were comparable. However, differences could be seen in the chromatographs (Fig. 4) of the scaled-up microwave and the classic prepared materials. This difference was evident for the scaled-up microwave prepared material where there was a shift in the peak associated with the low molecular weight species to higher molecular weight as well as an increase in the quantity present. This molecular weight increase though was not reflected in the \bar{M}_n , \bar{M}_w , and \bar{M}_w/\bar{M}_n values obtained for the two materials in Table 4.

Table 4. Comparison of neat resin properties

Property	TU15 (small batch)	TU15 (scaled-up)	Classic
Tg (T _m), °C: Initial [Cured]	123 (169, 223, 262) [308]	126 (170, 226, 266) [308]	139 [298]
250°C, Total % wt. Loss	0.05	0.31	0.00
300°C, Total % wt. Loss	0.07	0.39	0.08
350°C, Total % wt. Loss	0.16	0.52	0.30
\bar{M}_n , g/mole	2190	2350	2300
\bar{M}_w , g/mole	2640	2800	2790
\bar{M}_z , g/mole	3230	3360	3390
\bar{M}_w/\bar{M}_n	1.21	1.19	1.21
initial η^* @ 280°C, Pa·s	1.2	1.9	0.6
η^* at 280°C after 2hr hold, Pa·s	2.8	8.6	1.4

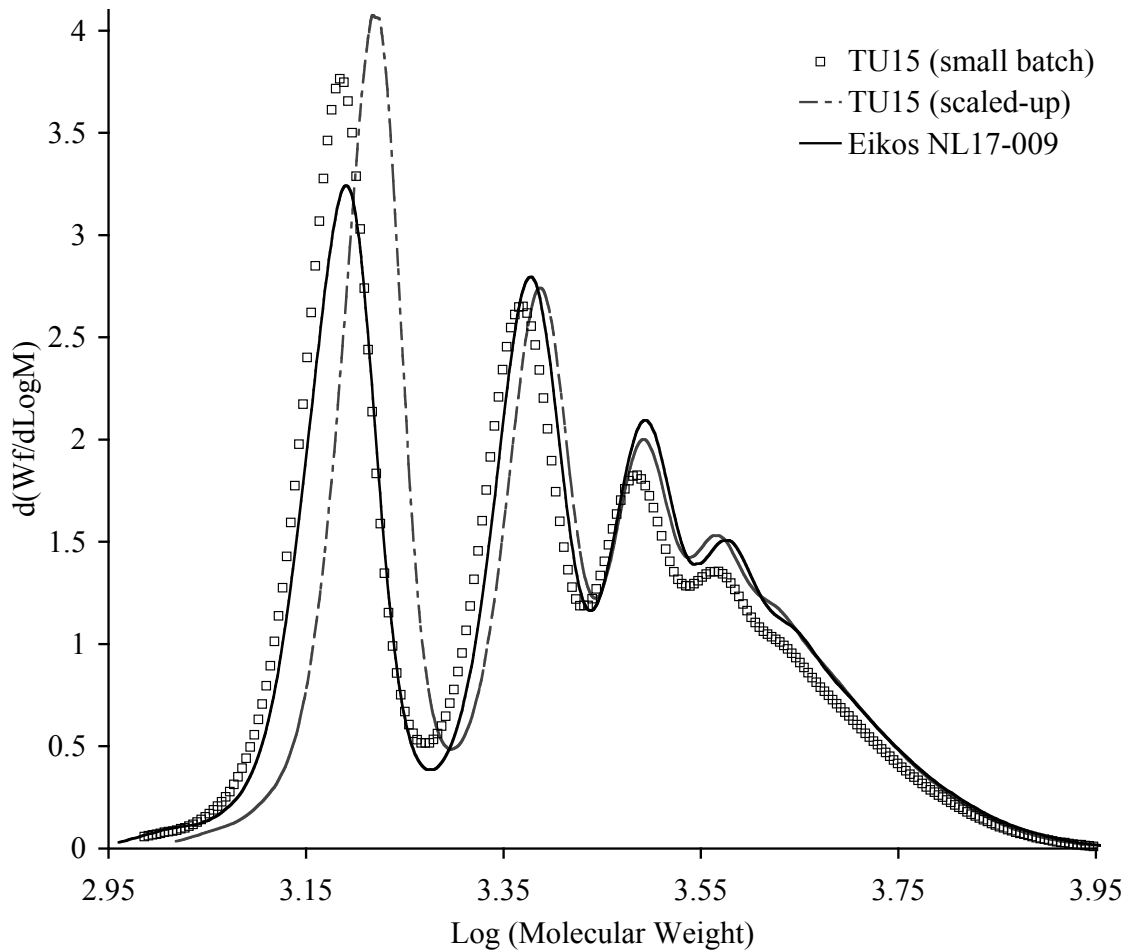


Figure 4. Chromatographs of PETI-298 prepared by microwave and classic solution based synthetic method.

Presumably the increase in the \bar{M}^* for the scaled-up microwave batch may be due to this molecular weight shift. The increase in the \bar{M}^* though was still well within the operating parameters of the equipment.

T650-35 8HS fabric laminates of PETI-298 [TU15 (scaled-up)] prepared by the microwave process were prepared by initially loading the dry powder into the injector and heating to 280°C under vacuum to degas the resin. The mold was placed in a platen press, heated to ~288°C and the resin injected under ~1.34 MPa hydrostatic pressure. The mold was then heated to 371°C for 1 hr, subsequently cooled to ~100°C and the pressure released. The laminates were ultrasonically scanned, machined into specimens and tested according to ASTM procedures. The microwave prepared PETI-298 exhibited processability comparable to that of the material

Table 5. PETI/un-sized T650-35 8HS Laminate Properties

Property	Test Temp., °C	Microwave Synthesis	Solution Synthesis
Fabric	-----	T650-35 8HS	T650-35 8HS
OHC Strength, MPa	23	287	260
	288	179	178
OHC Modulus, GPa	23	46	46
	288	43	43
SBS Strength, MPa	23	55.5	46.3*
	232	33.3	38.2*
	288	16.1	29.7*

* SBS data obtained on un-sized AS4-8HS fabric

prepared by the classic solution based synthetic route and provided laminates of excellent quality as evidenced by the C-scans and microscopic analysis. The as-processed laminates showed no microcracking as evidenced by microscopic examination. Fiber volumes ranged from 61 to 65% and void contents were less than 1% as determined by acid digestion for the microwave synthesized PETI-298/T650-35 laminates. Properties were determined at room temperature, 232, and 288 for PETI-298 (TU15 scaled-up)/un-sized T650-35 8HS laminates fabricated by RTM and are presented in Table 5. For comparative purposes, the properties of PETI-298/T650-35 laminates fabricated by RTM are included [2]. The PETI-298/T650-35 laminates had an average fiber volume of ~62% and a void content of ~2%. The data is not normalized for fiber volume. The PETI-298 (TU15 scaled-up) laminates exhibited OHC properties that were comparable to that of PETI-298 prepared by the classic solution based synthetic route. There was a noticeable drop-off in SBS strength at elevated temperature for the microwave prepared material. Unfortunately, no SBS data is available on PETI-298/T650-35 laminates, so SBS properties determined on AS4 fabric are included for comparison.

4. SUMMARY

PETI-298 was prepared in the solid state by microwave synthesis. Physical properties of the microwave prepared material were comparable to PETI-298 prepared via the classic solution route. However, slight differences in the GPC chromatographs of the microwave prepared material were observed in the low molecular weight range that affected the η^* relative to the classic amide acid route. Flat laminates exhibited comparable properties between the two methods with the exception of the SBS strength properties, which had a lower retention of strength at elevated temperature.

5. ACKNOWLEDGMENT

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